Title: **Synthesis and Photophysical Investigation of Precursors Designed for Carbon Sequestering Photocatalysts**

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OBJECTIVE(S):

The goal of this research is to recycle the combustion waste product carbon dioxide into a useful fuel or a chemical manufacturing feedstock (via solar energy conversion) instead of being given the opportunity to chemically alter the chemical composition of the atmosphere.

Although carbon dioxide may be converted via electrochemical methods, this method is not cost effective due to the high over-potential needed for conversion. New methods have been devised to enlist chromophores in photoinitiated supramolecular complexes to circumvent this problem. Functioning trimetallic photoinitiated supramolecular devices designed for homogeneous catalytic carbon dioxide conversion $\{[(bpy)_2Ru(BL)]_2MCl_2\}(PF_6)_5$ (where bpy = 2,2'-bipyridine and BL = 2,3-bis(2-pyridyl)pyrazine [dpp]; 2,3 – bis(2-pyridyl)quinoxaline [dpq]; or 2,3 – bis(2-pyridyl) benzoquinoxaline [dpb] and M = Ir^{III} or Rh^{III}) have been constructed and assessed by Brewer et al. [1,2, 3]

Homogenous catalysts, however, create time consuming and difficult product/catalyst separations. A solution to this issue is the attachment of a photocatalyst to a versatile solid support media, such as silica gel. This attachment can be accomplished by modification of the 2,2'-bipyridine terminal ligands to 4,4'-dicarboxyalato-2,2'-bipyridine and subsequent reactions with modified silica gels. Prior to the final construction step of the above proposed heterogeneous photocatalyst (attachment of the photochemical molecular device to the modified silica gel), precursors will be synthesized, fully characterized and photophysically studied.

ACCOMPLISHMENTS TO DATE:

- Laboratory space needed for the combined steady-state fluorescence and phosphorescence excited-state lifetime system was acquired and remodeled.

- A Jasco 4100 FT-IR (with ATR) was acquired and installed.

- New ligand purification routes were established to eliminate the use of copious amount of halogenated organic solvents used in prior purification methods.

- Monometallic Ir^{III} and Ru^{II} complexes have been synthesized via methods devised from modifications of literature methods.

- Began the multi-step synthesis of 4-carboxyalato-2,2'-bipyridine [cbpy] ligand.

FUTURE WORK:

- Completion of the cbpy ligand synthesis and subsequent characterization.

- Synthesis and characterization of the $\{[(dcbpy)_2Ru(BL)]_2MCl_2\}(PF_6)_5$ (where dcbpy = 4,4'-dicarboxyalato-2,2'-bipyridine and BL = 2,3-bis(2-pyridyl)pyrazine [dpp]; 2,3 – bis(2-pyridyl)quinoxaline [dpq]; or 2,3 – bis(2-pyridyl) benzoquinoxaline [dpb] and M = Ir^{III} or Rh^{III}) systems.

- Synthesis and characterization of $[(cbpy)(bpy)RuCl_2]$ and $[(cbpy)(bpy)Ru(BL)]^{2+}$ monometallic complexes.

LIST OF PAPERS PUBLISHED, U.S. PATENT/PATENT APPLICATION(S), CONFERENCE PRESENTATIONS, AWARDS RECEIVED AS A RESULT OF SUPPORTED RESEARCH, STUDENTS SUPPORTED UNDER THIS GRANT:

Student Supported: Melissa D. Wolfe

References

1. Molnar, S.M.; Nallas, G.; Bridgewater, J. S.; and Brewer, K. J. "Photoinitiated Electron Collection in a Mixed-Metal Trimetallic Complex of the Form $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}(PF_6)_5$ (bpy= 2,2'-bipyridine and dpb = 2,3 – Bis(2-pyridyl)benzoquinoxaline)" *J. Am. Chem. Soc.* 115 (7363-7373) **1993**.

2. Nallas, G. and Brewer, K. J. "Electrocatalytic Reduction of Carbon Dioxide by Mixed-Metal Trimetallic Complexes of the Form $\{[(bpy)_2Ru(BL)]_2IrCl_2\}(PF_6)_5$ where bpy= 2,2'-bipyridine and BL = 2,3 – Bis(2-pyridyl)quinoxaline (dpq) or 2,3 – Bis(2-pyridyl)benzoquinoxaline (dpb)".

3. Bridgewater, J.S.; Vogler, L.M.; Molnar, S.M. and Brewer, K.J. "Tuning the Spectroscopic and Electrochemical Properties of Polypyridyl Bridged Mixed-Metal Trimetallic Ruthenium(II), Iridium (III) Complexes: a Spectroelectrochemical Study." *Inorg. Chim. Acta.* 208 (179-188) **1993**.